

Chemical Bond Type, Atom Packing, and Superconductivity of $\text{YBa}_2\text{Cu}_3\text{O}_{8-x}$ and Na_xWO_3 .

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The $\text{YBa}_2\text{Cu}_3\text{O}_{8-x}$ superconductors are treated not as an ionic compounds but rather as an arrays of atoms featuring both covalent and metallic bonding. We accept as particle radii the positions of the principal maxima in the radial distribution functions of the charge density, which are very close to the known covalent and metallic radii of atoms while differing strongly from the traditional ionic radii. The graphic pattern of atomic packing in the lattices (approximate charge density map) reveals a number of features inherent in nonstoichiometric compounds. The network of atoms Y and Ba in medium Cu-O and of atoms Na in medium WO_3 may be considered not as a dopant but rather as the second component of the nanocomposite. The scheme of the onset of the superconducting state and possible methods of its verification are discussed.

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I. STRUCTURES

One of the reasons accounting for the difficulties involved in description of the mechanism of superconductivity of $\text{YBa}_2\text{Cu}_3\text{O}_{8-x}$ and of Na_xWO_3 may be an inadequate determination of the type of chemical bonding in these compounds. This situation ensues actually from the traditional use of ionic radii, whose definition was based on a number of empirical considerations and hypotheses. The radius of the O^{2-} ion is assumed equal to 1.4\AA [1, 2, 3], which automatically requires the use of ionic radii for the other atoms in $\text{YBa}_2\text{Cu}_3\text{O}_{8-x}$ and in Na_xWO_3 and determines the interaction type in the lattices. The Table lists such traditional ionic radii r_i [1, 2, 3]. Also presented are the radii r_{iq} and r_{aq} , which were calculated for free ions and atoms as the positions of the principal maxima in the radial distribution functions of the charge density [4], together with experimental values of the radii of atoms in covalent compounds and metals (r_c and r_m) [1, 2, 3].

As seen from the Table, the calculated atomic radii r_{aq} [4] are very close to the covalent, r_c , and metallic, r_m (coordination number 6), radii derived from exper-

imental data [1, 2, 3]. They are also in agreement with the minimum values of the Wigner-Seitz radii (the positions where the wave function gradient vanishes [5]). The radius $r_{iq} = 0.47\text{\AA}$ of the O^{2-} ion, however, not only differs strongly from the generally accepted value $r_i = 1.4\text{\AA}$ but turns out to be close to the radius of the free atom, $r_{aq} = 0.45\text{\AA}$, and to the covalent radius $r_c = 0.6\text{\AA}$, which is one half of the interatomic distance in the O_2 molecule. The paramagnetism of the O_2 molecule is a convincing argument for each of the resonance quantum states, $2p^2 - 2p^6$ ($\text{O}^{2+} - \text{O}^{2-}$), corresponding to a real physical property. In the chalcogen series (np^4) O, S, Se, Te, oxygen is the most favorably disposed towards formation of molecular structures.

The other ionic radii likewise differ so strongly in magnitude that the lattice structure with ionic radii r_{iq} cannot be stable. At the same time, use of the calculated (free), metallic, or covalent radii describes substantially better not only the structures of $\text{YBa}_2\text{Cu}_3\text{O}_{8-x}$ and Na_xWO_3 but a number of other perovskite lattices too, which requires a revision of atomic interactions as well. For instance, in the first case $2(r_{aqY} + 2r_{aqBa})\text{\AA} = 2(1.69 + 2 \times 2.06)\text{\AA} = 11.61\text{\AA} \sim c$ $c = 11.68\text{\AA}$ (c is the cell parameter of $\text{YBa}_2\text{Cu}_3\text{O}_7$ [6].) In the MeB_6 compound, the a lattice parameter does not change with a change of the metal as long as $a = 3.68\text{\AA} > 2r_{aqMe}$ but starts to increase when $2r_{aqMe}$ exceeds a [7]. Note that bonding in the B_6 octahedra remains covalent. The tungsten bronze $\text{Na}_{0.05}\text{WO}_3$ switches to superconducting state at $T_c = 91\text{K}$ [8]. In this case, $a = 3.78\text{\AA} > 2r_{aqNa}$. If, however, Na is replaced by Rb or Cs, for which $a < 2r_{aqRb}$ or $2r_{aqCs}$, T_c drops to a few K [8]. No replacement of Na with Li or Ag ($r_{aqNa} > r_{aqLi,Ag}$) was attempted. The network of atoms Na in medium WO_3 may be considered not as a dopant but rather as the second component of the nanocomposite. Figures 1a and 1b shows the cell of WO_3 constructed using for W the atomic radius r_{aqW} .

TABLE

ion	W ⁶⁺	Na ¹⁺	Cu ²⁺	Ba ²⁺	Y ³⁺	O ²⁻
$r_i\text{\AA}$ [1, 2, 3]	0.60	1.02	0.73	1.36	0.90	1.4
$r_{iq}\text{\AA}$ (calculated)[4]	0.57	0.28	0.32	0.87	0.64	0.47
atom	W	Na	Cu	Ba	Y	O
$r_{aq}\text{\AA}$ (calculated) [4]	1.36	1.72	1.19	2.06	1.69	0.45
$r_c\text{\AA}$ (covalent) [1, 2, 3]	1.30	1.54	1.17	1.98	1.68	0.60
$r_m\text{\AA}$ (in metal) [1, 2, 3]	1.37	1.86	1.28	2.17	1.78	—

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For the atomic radius of oxygen we took $\sim 0.55\text{\AA}$ which is close to the covalent value. Only for this value of the oxygen radius can the perovskite cavity accommodate freely a Na atom to make possible the Jahn–Teller effect (formation of Na_2 molecules with paired electrons); there will be no such effect, however, if the Rb and Cs atoms are compressed. Figures 1c and 1d present sections of the NaWO_3 cell along the \vec{A} and \vec{B} directions.

Considering chemical bonding to result from interactions of the ionic, metallic, and covalent types, one has to accept in this case predominance of metallic bonding in the "filler"—atoms of the metal, which only weakly interact with the WO_3 "matrix" (insulator). This conclusion correlates well both with geometric considerations and with the concept of nonstoichiometric compounds to which Na- WO_3 belongs.

The pattern for $\text{YBa}_2\text{Cu}_3\text{O}_8$ will be as consistent geometrically if one invokes the atomic rather than ionic radii for the metal atoms and the radius 0.55\AA for the oxygen atoms. Figures 2a and 2b displays a cell of the Cu–O "matrix", which in this case (without the "filler", i.e., the Y and Ba atoms), in contrast to that of WO_3 , is certainly unstable. The atomic positions and the cell parameters of $\text{YBa}_2\text{Cu}_3\text{O}_7$ ($a = 3.88\text{\AA}$, $b = 3.83\text{\AA}$, and $c = 11.68\text{\AA}$) were taken from [6].

II. SUPERCONDUCTIVITY

A characteristic feature of a number of HTSC compounds is the onset of superconductivity when univalent atoms (inherently not superconductors), e.g., Na [8] or Ag [9, 10] are inserted into nonmetallic matrices. These systems are typically unstable. Figure 3 illustrates schematically the situation with $\text{Na}_{0.05}\text{WO}_3$. For $a > 2r_{aq\text{Na}}$, Na_2 molecules form in the lattice through the Jahn–Teller effect, which is impossible for the Rb and Cs atoms. A transition to the divalent system has occurred ("two-center" electron pairs appeared), with no constraints on superconductivity (as in the case with univalent atoms which do not have paired electrons) present any longer. As seen from Figure 2c, a similar effect is observed for the Y component in $\text{YBa}_2\text{Cu}_3\text{O}_8$. In this case, both metallic components (Y_2 and Ba) may be considered as consisting of particles with electron pairs. Chains of such particles form a 3D network in the Cu–O matrix (Figure 2c, 2d). A dilute gas of diatomic molecules, for instance, of Na_2 in $\text{Na}_{0.05}\text{WO}_3$ (Figure 3), and, conceivably, in pressure-metallized condensates of inert gases (IG), for example, of Xe_2 in xenon, forms a disordered "cobweb" of superconducting filaments in an insulating matrix [11, 12]. But while the $\text{Na}_{0.05}\text{WO}_3$ superconductor is unstable against formation of domains of conventional tungsten bronze NaWO_3 , in xenon the Xe_2 molecules form an equilibrium gas.

Consider the formation of a condensate at $T = 0$ as particles with electron pairs approach one another ever closer (i.e., as their concentration N increases). These

may be, for instance, "one-center" electron pairs in Hg atoms or "two-center" pairs in Na_2 molecules. Because at equilibrium the condensate is a superconductor, it also contains electron pairs, but they exist here as "many-center" bosons, i.e., Cooper pairs. These "composite" bosons could conceivably form of atomic or molecular electron pairs whose binding energy decreased, and the size and overlap increased continuously as k , the effective dielectric constant of the medium, grew with increasing N . In the Hg metal (the ionization potential $IP = 10\text{eV}$), the decrease of the pair binding energy is estimated to be $(IP/kT_c) \sim 10^4$. In the HTSC materials, in which the concentration of particles with paired electrons is lower than that in metals as a result of dilution by a second component, the matrix, the effective dielectric constant is smaller, and T_c , higher. This constant is still smaller in IGs. In other words, T_c may depend on concentration but not the bond energy and have an optimum in N , and decay of electron pairs and formation of metal may be preceded by Bose condensation [12].

Following the process of Bose condensation of such electron pairs with variation of N in many-component chemical compounds is anything but a simple problem. This could be possibly realized, however, under pressure-induced metallization of "one-component" IGs, which are assumed to contain diatomic excited (excimer) molecules, for instance, Xe_2 (atomic diameter 4.6\AA) immersed in a medium of Xe atoms in the ground state ($5p^6$, diameter 1.2\AA [4]) (atom-molecule mixture) [11, 12, 13, 14]. Both the pair excited states and atoms in ground state ("quantum cavities and channels") in IGs are as real as the paramagnetism of the O_2 molecules. They are counterparts of quantum states of atoms ($np^5(n+1)s^1$ and np^6) (coexistence or superposition of two condensates based on own quantum state). Such an atom-molecule mixtures, perhaps, exist in ^4He and ^3He . The dielectric constants of the IGs are on the order of a few units, so that the electron pairs should be bound stronger than those in an HTSC. By now, xenon has been reliably established to undergo metallization [15]. Only its optical parameters have, however, been studied, while the magnetic characteristics (superconductivity) did not attract interest. Superconductivity was observed to set in under pressure in sulfur ($T_c = 17\text{K}$ [16]) and in oxygen ($T_c = 0.6\text{K}$ [17]). Both sulfur and oxygen are, however, paramagnets, so that strong local magnetic fields could suppress the superconductivity.

The validity of the considerations bearing on the IGs (condensates of particles with electron pairs in a medium of ground-state atoms) may be argued for by some anomalous properties of palladium. Palladium (Pd: ground state (g.s.) $4d^{10}5s^0$, $2r_{aq} = 1.2\text{\AA}$, excited state (e.s.) $4d^95s^1$) in the form of a condensate ($2r_m = 2.75\text{\AA}$) correlates with a strongly metallized IG [18]. Unlike IGs, Pd has a low excitation energy ($\sim 1\text{eV}$). However, the Pd lattice still has some atoms in the ground state ("quantum cavities and channels"),

which becomes manifest, for instance, in the anomalously high permeability of palladium for hydrogen (see, also Nb (g.s.: $4d^4 5s^1$ - e.s.: $4d^5 5s^0$, $2r_{aq} = 1.50\text{\AA}$) and Ta (g.s.: $5d^3 6s^2$ - e.s.: $5d^5 6s^0$; $2r_{aq} = 1.56\text{\AA}$).

As the Pd lattice is extended (N decreases) through incorporation of foreign atoms (Li, Ag, Cu, Au, B, C, N, H etc.), Pd becomes superconducting with T_c of up to 17K [19, 20]. The same effect take place for compounds Nb-C, Nb-Sn, Nb-Ge ($T_c \sim 11\text{K} \div 23\text{K}$).

The insulator–superconductor–metal transition driven by variation of the concentration of particles with electron pairs can be studied both on one-component systems (compression of an IG or "extension" of Pd) and, naturally, on HTSC materials. The latter are usually nonstoichiometric compounds, so that the type of chemical bonding prevailing in their components and between them depends critically on the states in which the atoms reside [21].

Thus, the major technological difficulty in the way of developing HTSC materials consists in preparing stable systems of particles with paired electrons (for instance, divalent atoms or molecules) in concentrations at which the electron pairs already are capable of tunneling (Bose condensation) while not yet separating into single elec-

trons, either as a result of conventional chemical interactions or through a decrease in their binding energy in an effective dielectric medium. Such an intermediate state corresponds to a "stretched" or "diluted" substance, which can be stabilized by using solid solvents as matrices. In some cases such nonequilibrium concentrations are possibly "frozen" by chance fluctuations in the technology of synthesis [8, 9, 10]. Low and equilibrium concentration of particles with two paired electrons may exist in some compounds (like $\text{Ag}_2[\text{Ag}_3\text{Pb}_2\text{O}_5]$) with 1D channels [10]. In searching for efficient methods of structural stabilization (with help of some amount of inert particles as "additional diluent" (third component), for instance), a better understanding of the interactions in the structure of each component is of crucial importance. Such methods of stabilization can be found only by using realistic atomic and ionic radii rather than conventional quantities, which are nothing else but a consequence of postulated bonding types. The matrices in such nanocomposites also exist in an unusual state because of the unusual structure and contact interaction with the second component. This complicates greatly the investigation and description of such systems.

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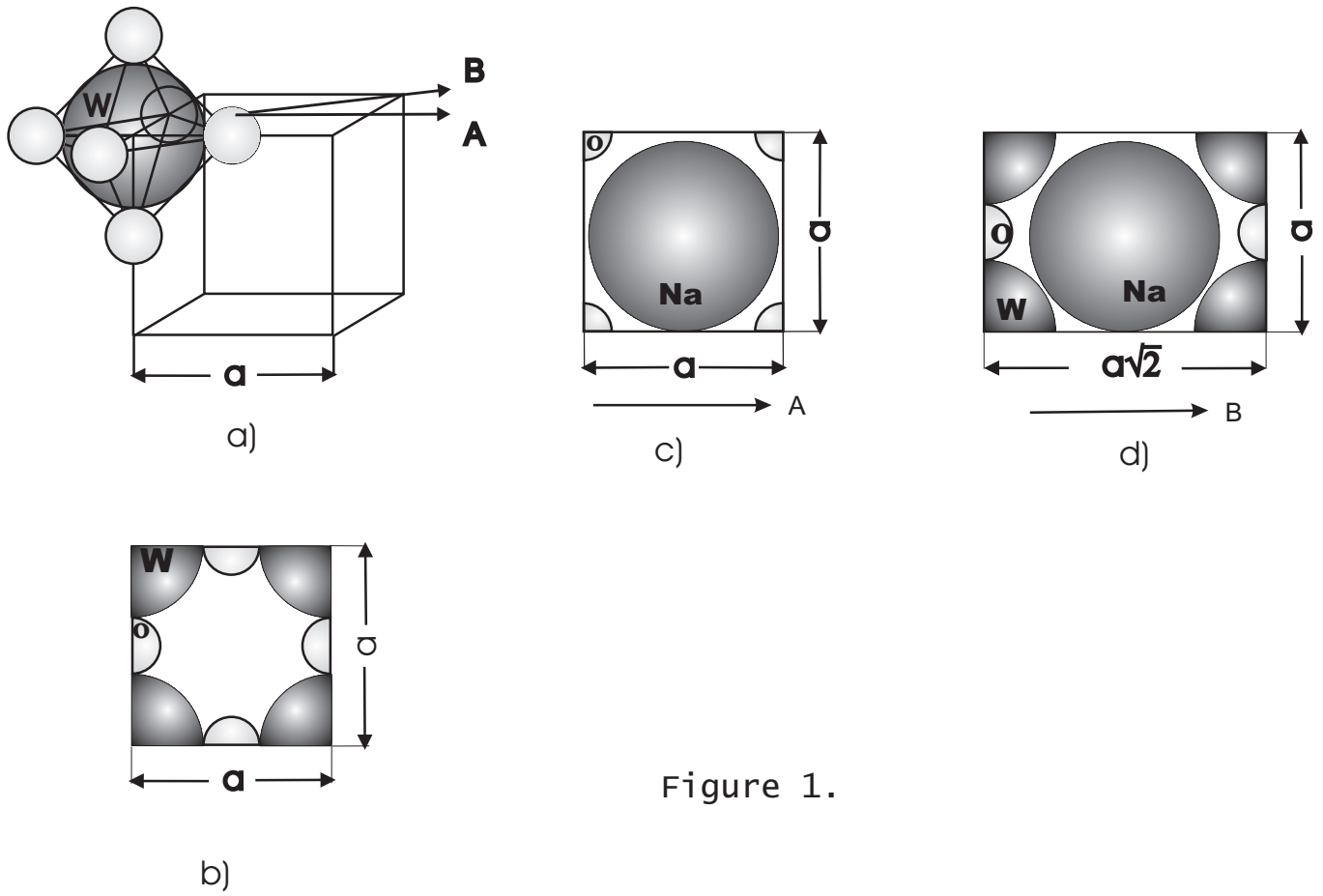


Figure 1.

FIG. 1:
 (a) WO_3 cell;
 (b) Side face of the WO_3 cell;
 (c) Section of NaWO_3 cell along the \vec{A} direction;
 (d) Section of NaWO_3 cell along the \vec{B} direction.

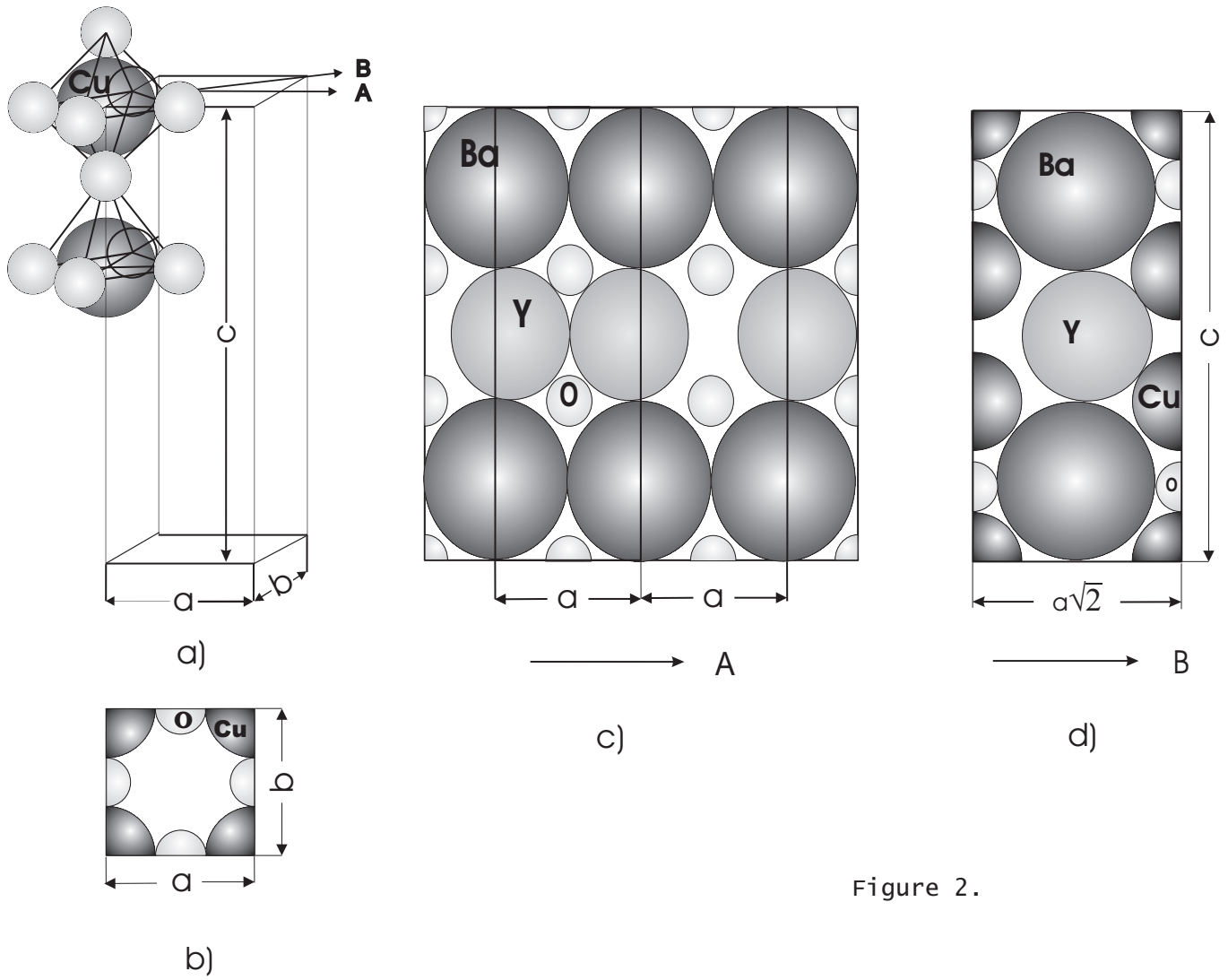


Figure 2.

FIG. 2:
 (a). $\text{YBa}_2\text{Cu}_3\text{O}_8$ cell;
 (b) Side face of the $\text{YBa}_2\text{Cu}_3\text{O}_8$ cell;
 (c) Section of $\text{YBa}_2\text{Cu}_3\text{O}_8$ cell along the \vec{A} direction;
 (d) Section of $\text{YBa}_2\text{Cu}_3\text{O}_8$ cell along the \vec{B} direction.

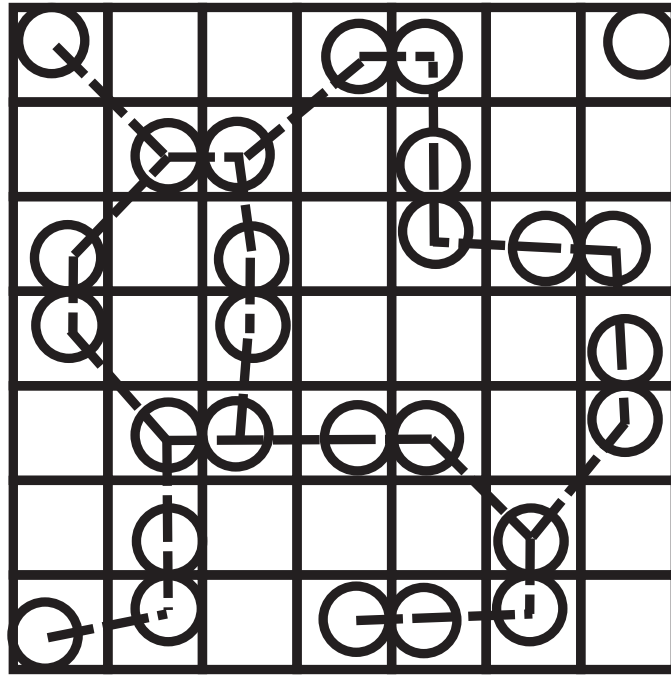


Figure 3.

FIG. 3:
Schematic arrangement of $\text{Na}_2(\text{Xe}_2)$ molecules in $\text{Na}_{0.05}\text{WO}_3$ (Xe under pressure). A variant of divalent impurity in insulator. Dashed lines: "cobweb" [11, 22] of superconducting filaments of $\text{Na}_2(\text{Xe}_2)$ molecules. The system $\text{Na}_{0.05}\text{WO}_3$ is unstable against formation of metallic domains of the tungsten bronze Na_1WO_3 . A "gossamer" of superconducting filaments in insulator supposed to be in cuprates (Fig.2)[23].